A Langmuir Monolayer with a Nontraditional Molecular Architecture

**Qun Huo,[†] Stoyan Russev,[‡] Takeshi Hasegawa,[§] Jujiro Nishijo,[§] Junzo Umemura,[⊥]
Germain Puccetti,[†] K. C. Russell,[†] and Roger M. Leblanc*,[†]**

Contribution from the Center for Supramolecular Science, Department of Chemistry, University of Miami, 1301 Memorial Drive, Coral Gables, Florida 33124, Faculty of Physics, Department of Solid State Physics, Sofia University, Sofia, Bulgaria, Kobe Pharmaceutical University, Motoyama-kita, Higashinada-ku, Kobe 658-8558, Japan, and Institute for Chemical Research, Kyoto University, Uji 611-0011, Japan

Received December 2, 1998

Abstract: In the traditional concept, a stable Langmuir monolayer can be formed from amphiphilic molecules at the air−water interface with their hydrophobic alkyl chains oriented toward the air and the polar moieties embedded in the water. The intermolecular interactions between the polar moieties and the water subphase as well as the van der Waals interactions between the alkyl chains are requisite to hold together the molecules of the ordered Langmuir monolayers. Pure hydrocarbon chains without any polar moieties cannot form a Langmuir monolayer. In contrast to this traditional concept, we now report the discovery of an unusual Langmuir monolayer formed from a disubstituted urea lipid molecule (PDA-UR). The unique property of this monolayer exists in the fact that the polar moiety of the lipid molecule is actually suspended in the air phase while one of the hydrophobic tails is in contact with water. The existence of such a nontraditional monolayer is attributed to the strong hydrogen bonding network formation between the urea functional groups in the air phase. This unusual Langmuir monolayer model is soundly supported by various experimental investigations, which include the surface pressure−area isotherm and ellipsometry measurements, FT-IR and UV−vis absorption spectroscopic studies, as well as Brewster angle and scanning tunneling microscopic observations.

Introduction

Hydrogen bonding plays a crucial role in biological systems and has kept attracting keen interest from chemists. Among all the noncovalent interactions, the strength, directionality, and synthetic feasibility place hydrogen bonding at the center of many research areas aimed at the design of supramolecular assemblies.[1] Highly organized and well-defined supramolecular structures such as linear tapes, crinkle tapes, or rosettes can be formed through the complementary hydrogen bonding between barbiturates and melamines.[2] More recently, the linear hydrogen bonding network formed from melamine or barbiturate lipids in Langmuir monolayers has also been investigated.[3−5] These studies provide a novel approach in the design and creation of well-organized supramolecular species in two dimensions.

We recently demonstrated that the linear hydrogen bonding network formed between a melamine lipid with its complementary components from the aqueous subphase can control the polymerization of the diacetylene alkyl chain attached to the melamine.[6] The resulting polydiacetylene Langmuir film only exhibits a blue form absorption band rather than a transition from blue to red, as observed from other polydiacetylene monolayers. It is believed the existence of the hydrogen bonding network forces the polydiacetylene chain to remain linear and obtain efficient $\pi-\pi$ electron conjugation.[6]

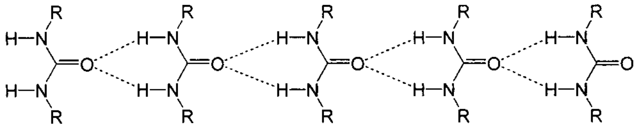


Figure 1. An illustration of linear hydrogen bonding self-assembling network in the solid state formed between urea functional groups.

Substituted ureas and vinylogous ureas have also been reported to form linear hydrogen bonding α-networks via the carbonyl group of one urea and the anti-hydrogen atoms of the nitrogen atoms of a neighboring urea (Figure 1) in the solid state.[7] The typical distance between the urea substituent groups in the α-network is around 4.5−5 Å. It is known that the topochemical photopolymerization of diacetylenes requires a repeating distance of ≤5 Å between diacetylene groups to take place.[7] On the basis of this information, we have designed and synthesized a urea derivative, PDA-UR, with two 10,12-pentacosadiynoic acid (PDA) chains attached symmetrically to the urea functional group (Scheme 1). Three questions were put forward before the study: Could this PDA-UR molecule form a Langmuir monolayer at the air−water interface like other amphiphilic molecules? Would the urea functional groups in the lipids form a linear hydrogen bonding network similar to what was observed in the solid state? How would the hydrogen

---

* To whom correspondence may be addressed.

[†] University of Miami.

[‡] Sofia University.

[§] Kobe Pharmaceutical University.

[⊥] Kyoto University.

(1) Lehn, J.-M. *Supramolecular Chemistry*; VCH: New York, 1995.

(2) Extensive literatures are not listed here. For a general review of studies on hydrogen bonding self-assembling in solution and solid state, refer to: MacDonald, J. C.; Whitesides, G. M. *Chem. Rev.* **1994**, *94*, 2383.

(3) Koyano, H.; Bissel, P.; Yoshihara, K.; Ariga, K.; Kunitake, T. *Chem. Eur. J.* **1997**, *3*, 1077.

(4) Weck, M.; Fink, R.; Ringsdorf, H. *Langmuir* **1997**, *13*, 3515.

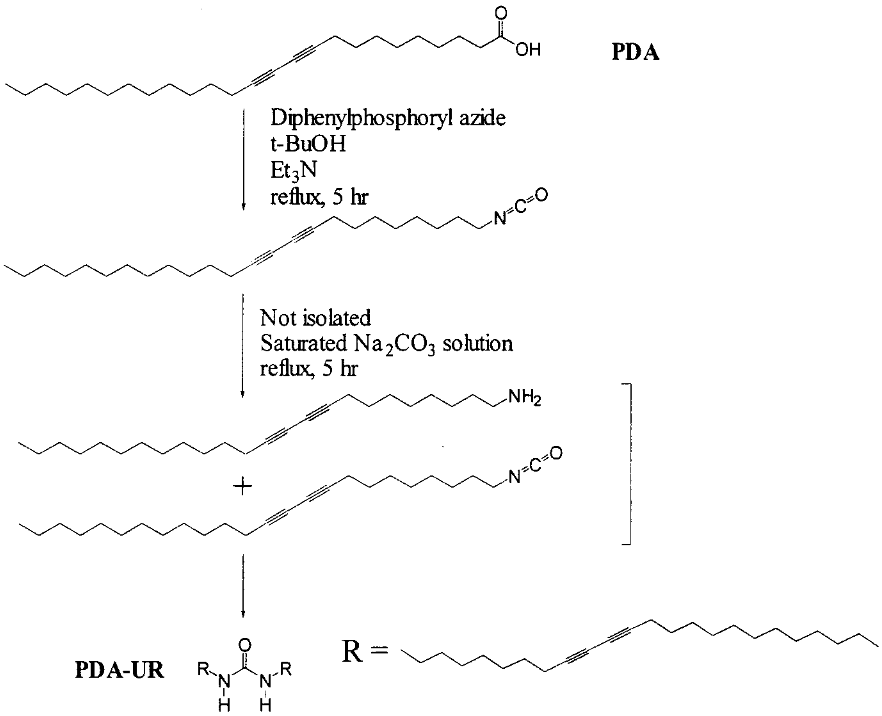
(5) Huo, Q.; Russell, K. C.; Leblanc, R. M. *Langmuir* **1998**, *14*, 2174.

(6) Huo, Q.; Russell, K. C.; Leblanc, R. M. *Langmuir* **1999**, *15*, 3972. Previous work on polydiacetylenes has been summarized here.

(7) Coe, S.; Kane, J. J.; Nguyen, T. L.; Toledo, L. M.; Wininger, E.; Fowler, F. W.; Lauher, J. W. *J. Am. Chem. Soc.* **1997**, *119*, 86.

10.1021/ja984158j CCC: $19.00

Scheme 1. The Structure and Synthesis of PDA-UR from PDA



bonding between the urea functional groups affect the monolayer properties and the polymerization of the diacetylene groups?

Experimental Section

Materials. The chemicals and solvents used for synthesis and surface chemistry studies were purchased from Aldrich Chemical Co. (Milwaukee, WI) and used without further purification. 10,12-Pentacosadiynoic acid (PDA) was purchased from GSF Chemical Co. (Powell, OH) and recrystallized from petroleum ether before use. The melting point was taken on a Thomas-Hoover melting point apparatus and is uncorrected. The ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were obtained from a Varian VXR 400 MHz spectrometer. The mass spectrum was recorded on a research VG-Trio 2000 mass spectrometer. The combustion analysis was conducted by Atlantic Microlab Inc. (Norcross, GA).

Synthesis of *N*′-Di-10,12-pentacosadiynoic Urea (PDA-UR). Crystallized 10,12-pentacosadiynoic acid (1.91 g, 5.0 mmol) was dissolved in a mixture of diphenylphosphoryl azide (DPPA, 1.38 g, 5.00 mmol), triethylamine (1.6 mL, 12.0 mmol), and *tert*-butyl alcohol (100 mL). The reaction mixture was brought to reflux for ca.. 5 h. After evaporation of the solvent in vacuo, saturated aqueous sodium bicarbonate (50 mL) was added to the residue and the suspension was brought to reflux for another 5 h. After the reaction mixture was cooled to ca. 60 °C, the light blue solids were suction filtered and vacuum dried for 1 h. The crude product was recrystallized from hot butanol (ca. 300 mL) to give white crystals (yield 80%). Mp: 112−117 °C. ^{1}H NMR (CDCl$_3$): δ 0.85 (t, 6H), 1.18−1.55 (m, 64 H), 2.21 (t, 8H), 3.12 (q, 4H), 4.14 (t, 2H). ^{13}C NMR (CDCl$_3$): δ 14.2, 19.4, 22.6, 26.8, 28.0−30.2 (m), 32.0, 40.8, 66.0. FABMS: calcd for $C_{49}H_{84}N_2O$ *m/z* 716.7, found 718.0 ($M^+ + 1$). Combustion analysis: calcd for $C_{49}H_{84}N_2O$ C 82.06, H 11.80, N 3.91; found C 81.75, H 11.80, N 3.98.

Methods for Surface Pressure−Area Measurements and UV−Vis Absorption Spectroscopic Studies at the Air−Water Interface. HPLC grade chloroform was obtained from Fisher Scientific Co. Pure PDA or PDA-UR was dissolved in a mixture solvent chloroform/MeOH (5/1, v/v) to a concentration of 1.0 mM. The water used for the monolayer study was purified by a Modulab 2020 water purification system (Continental Water Systems Corp., San Antonio, TX). The water has a resistance of 18 MΩ·cm and a surface tension of 72.6 mN/m at 20 °C. The injected volume was 60 μL for both PDA and PDA-UR solution. After spreading the sample, the solvent was allowed to evaporated for 10 min. The compression rate was set at 5 Å^2/(molecule·min).

All the experiments were conducted in a clean room class 1000 where the temperature (20 ± 1 °C) and the humidity (50 ± 1%) are controlled. The Langmuir trough used for the surface pressure measurements was a KSV minitrough, model 2000. The trough dimensions were 7.5 × 30 × 1 cm^3. The surface pressure was measured by the Wilhelmy method. The resolution of the Wilhelmy balance is ±0.01 mN/m. All the isotherm measurements were repeated three times and the isotherm presented is the average of three measurements. The deviation between the average isotherm and any of the three individual isotherms is ±1 Å^2/molecule. UV−vis spectra of the monolayer at the air−water interface were measured using a modified Hewlett-Packard 8452A diode array spectrophotometer through a quartz window in the center of the KSV minitrough. The UV lamp of the spectrophotometer is also the light source for the irradiation. The power of the light on the monolayer at 254 nm is 0.6 W/m^2.

Brewster Angle Microscopic Study. For the Brewster angle microscopic studies of the PDA-UR monolayer, a Nippon trough (5 × 47 × 1 cm^3), equipped with a moving wall system (NL-LB140S-MWC, Nippon Laser & Electronics Lab., Nagoya, Japan),was used, to which was connected a Brewster angle microscope (BAM) (EMM633S, Nippon Laser & Electronics Lab., Nagoya, Japan), a helium−neon laser (wavelength 632.8 nm and power 10 mW), and a CCD camera. The images from the CCD were captured and digitized using a digital video capture mode (Snappy video Snapshot, Rancho Cordova, CA) for further analysis. The surface topography of the PDA-UR monolayers in the water subphase was visualized and recorded during the compression. The BAM images were analyzed at different surface pressures using the digital video capture mode mentioned above. The images presented in this work have dimensions of 400 × 400 μm^2.

Ellipsometric Measurements of the PDA and the PDA-UR Monolayers. The ellipsometric measurements of the PDA and the PDA-UR monolayers were conducted using the experimental setup as reported in the literature.[8,9] The change of both ellipsometric angle Δ and ψ^8 was monitored during the compression. Up to four compression/decompression cycles were performed and only the ellipsometric angle

---

(8) Azzam, R. M. A.; Bashara, N. M. *Ellipsometry and Polarized Light*; North-Holland: Amsterdam, 1977.

(9) Russev, S. C.; Arguirov, T. V. *Rev. Sci. Instrum.* **1999**, *70*, 3077.

Table 1. Optical Constants for Bulk Samples Used for the Calculation of Molecular Orientation Angles

wavenumber/cm^{-1}	air	PDA-UR monolayer	gold
2850 (ν_s(CH$_2$))	1.0	1.47 + 0.423i	0.738 + 23.58i
2918 (ν_a(CH$_2$))	1.0	1.47 + 0.594i	0.711 + 23.08i

(Δ)−area isotherms of the first compression of each compound are presented here. The changes of ellipsometry angle ψ in both PDA and PDA-UR monolayers are small and have been used to estimate the refractive index (*n*) of the corresponding monolayer. The thickness (*d*) of the monolayer was calculated based on the refractive index of the monolayer and the change of ellipsometry angle Δ between the surface pressure of nil and the collapse point using the method as described in the literature.[8]

FT-IR Spectroscopy Study of PDA-UR LB Films. (1) LB film deposition: PDA-UR monolayers were prepared on a water surface at surface pressures of 2.0 and 10.0 mN/m in a dark enclosure to prevent polymerization of PDA-UR by UV light. The monolayers were transferred on a gold-evaporated glass slide by the vertical dipping method to form one-monolayer LB films. The thickness of the gold layer was 300 nm, which was deposited on a chromium layer that stabilizes the gold layer during the evaporation process. The LB depositions were performed on a Kyowa Interface Science (Saitama, Japan) HBM LB film apparatus at 25 °C. The subphase water was pure water, and the pH of the water was ca. 6.0.

(2) Infrared spectra measurements: Infrared reflection−absorption (IRRA) spectra were measured by a Nicolet (Madison, WI) Magna 850 FT-IR spectrometer with a deuterated triglycine sulfate (DTGS) detector at a modulation frequency of 5 kHz. For the reflection measurements, a Harrick Scientific (Ossining, NY) RMA-1DG/VRA variable angle reflection attachment was used in the FT-IR sample room. The angle of incidence was fixed at 80° from the surface normal. The p-polarized infrared ray for the IRRA measurements was generated through a Hitachi (Tokyo, Japan) wire grid infrared polarizer made of AgBr. The measurement temperature was maintained at 25 °C.

A spectrum of bulk PDA-UR was measured by the KBr pellet method for evaluating extinction coefficients. More detail of this evaluation process is described in the literature.[10]

(3) Calculation of molecular orientation angle: The molecular orientation angle was evaluated from IRRA spectra with the use of a theory deduced by Hasegawa et al.[10,11] For the detailed procedure of this calculation, the readers can refer to the literature. The optical constants used for the calculation are summarized in Table 1. When the extinction coefficients were evaluated, the band location of the asymmetric CH$_2$ stretching vibration (ν_a(CH$_2$)) band was noticed, since the band at 2918 cm^{-1} suggested that the monolayer was in a transition process between all-trans and gauche conformations. This wavenumber is found when a cadmium stearate monolayer is at 80°.[10] Therefore, the extinction coefficients of the cadmium stearate monolayers at this temperature were cited as the standard coefficients for the symmetric CH$_2$ stretching vibration (ν_s(CH$_2$)) and the ν_a(CH$_2$) bands: 0.175 and 0.250, respectively. Then, the extinction coefficient of the ν_s(CH$_2$) band of the PDA-UR monolayer was evaluated to be 0.423 by taking the number of methylene groups into account (38 and 16 for PDA-UR and stearic acid, respectively). In the same manner, the estimated coefficient of the ν_a(CH$_2$) was 0.594 (Table 1).

Thickness and surface area were used for the molecular orientation analysis as described in the literature.[11,12] The thickness of the PDA-UR used for the calculation monolayer was 7.0 nm, which was provided by ellipsometry measurements. The surface area (density) was taken from the surface pressure−area isotherm of a PDA-UR monolayer. The experimentally obtained surface areas of the monolayer at 2.0 and 10.0 mN/m were 24.4 and 17.6 Å^2/molecule, respectively.

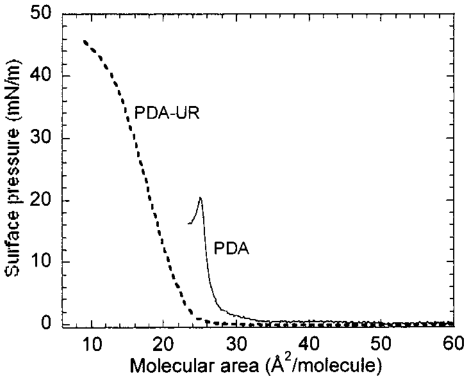


Figure 2. The surface pressure−area isotherms of PDA and PDA-UR monolayer on the pure water subphase (pH 5.8).

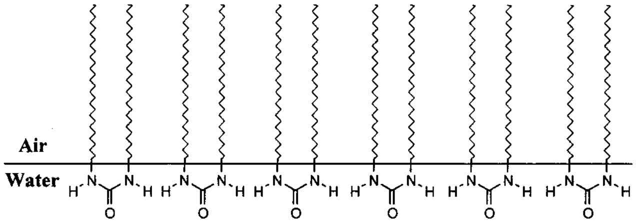


Figure 3. A model of the PDA-UR monolayer based on the traditional concept of Langmuir films.

Results and Discussion

I. Surface Pressure−Area Isotherm Studies. The surface pressure−area isotherm of PDA-UR has been measured, along with the surface pressure−area isotherm of PDA as a comparison (Figure 2). The isotherm of PDA agrees with our previous studies[6] and the literature report.[13] The limiting molecular area of PDA by the extrapolation of the isotherm at nil surface pressure is 27 Å^2/molecule. On the other hand, the isotherm of PDA-UR is quite striking. The limiting molecular area obtained for PDA-UR is only about 23 Å^2/molecule. PDA-UR looks very much like a traditional amphiphilic molecule, with a urea polar moiety and two hydrophobic alkyl chains. According to the traditional concept of a Langmuir film, one might easily assume that the PDA-UR molecule will form a monolayer with its urea polar moiety embedded in the water and the two alkyl tails intruded to the air, as illustrated in Figure 3. According to this configuration, then the limiting molecular area of PDA-UR should be around 42 Å^2/molecule instead of the observed 23 Å^2/molecule, since the cross section of one alkyl chain is approximately 21 Å^2/molecule.

Since PDA-UR is insoluble in water (even at 100 °C!), it is very unlikely that any molecules are lost in the subphase during the compression, leading to the observation of a small molecular area. This hypothesis is supported by the kinetic study of the monolayer. When compressed to different surface pressures, 10, 20, 30, and up to 40 mN/m, the monolayer can be held in the same surface pressure for at least 1 h without any observable barrier shift (Figure 4). This study strongly supports the observation that no PDA-UR molecules are lost into the subphase during the compression.

In the meantime, the compression−decompression studies have brought up more insights into the stability of the PDA-UR monolayer. When compressed to a surface pressure of 25 mN/m, the monolayer was decompressed (Figure 5, curves 1 and 2). The decompression isotherm is significantly deviated from the compression isotherm. When the barriers returned to

---

(10) Hasegawa, T.; Takeda, S.; Kawaguchi, A.; Umemura, J. *Langmuir* **1995**, *11*, 1236.

(11) Hasegawa, T.; Hatada, Y.; Nishijo, J.; Umemura, J.; Huo, Q.; Leblanc, R. M. *J. Phys. Chem. B* **1999**, *103*, 7505.

(12) Hasegawa, T.; Myrzakozha, D. A.; Imae, T.; Nishijo, J.; Ozaki, Y. J. *J. Phys. Chem. B* **1999**, *103*, 11124.

(13) Mino, N.; Tamura, H.; Ogawa, K. *Langmuir* **1991**, *7*, 2336.

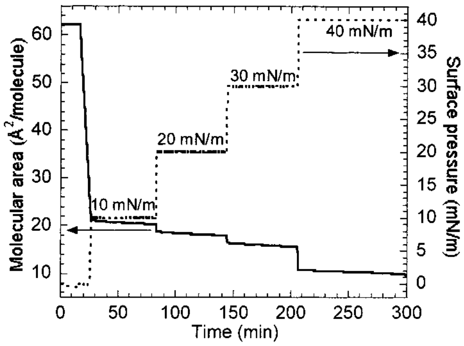


Figure 4. The kinetic study of the PDA-UR monolayer on the pure water subphase (EnDash−, molecular area; •••, surface pressure).

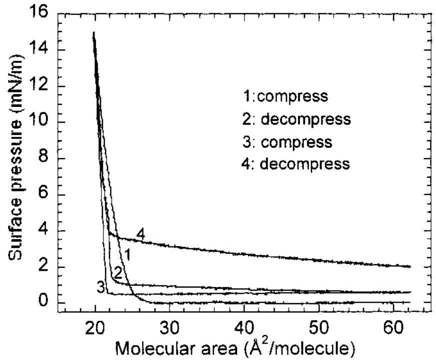


Figure 5. The compression and decompression isotherms of the PDA-UR monolayer.

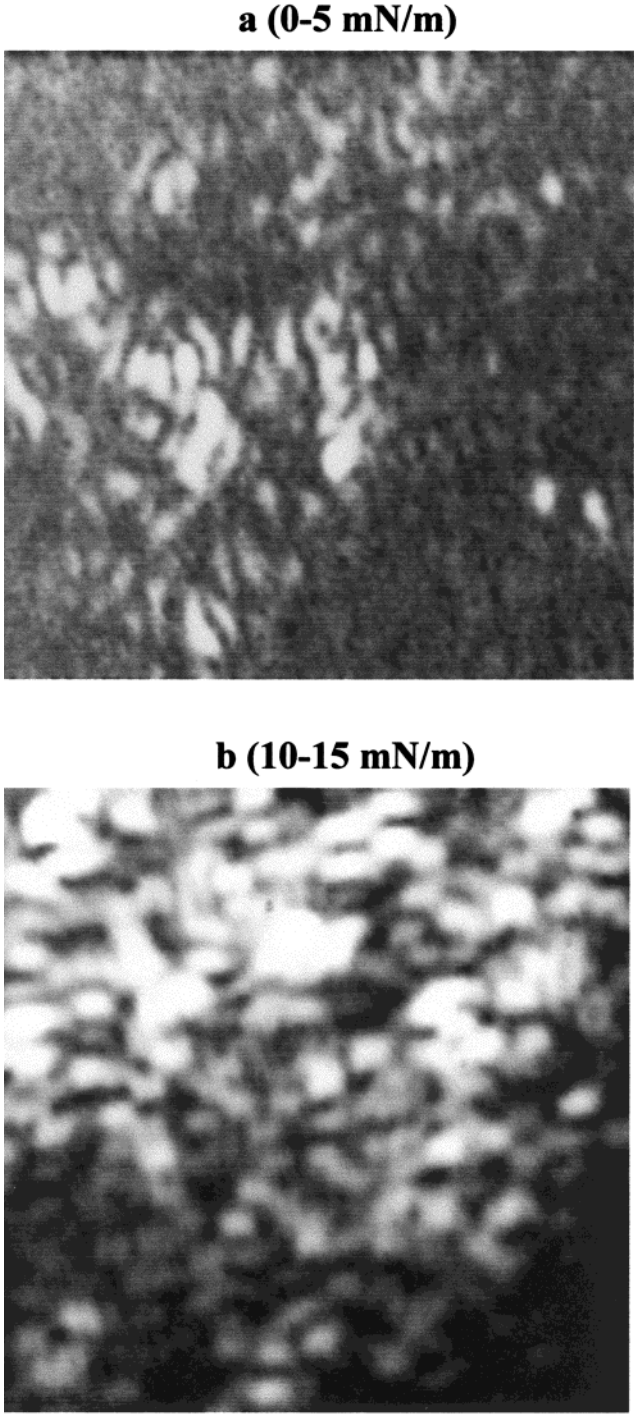


Figure 6. The Brewster angle microscopy images of the PDA-UR monolayer on the water subphase at two different compression stages (a, 0−5 mN/m; b, 10−15 mN/m; both images have a size of 400 × 400 μm).

the maximum area position, the surface pressure did not return to nil. It remained at about 1 mN/m. The same phenomenon was observed in the second cycle of compression and decompression isotherms (curves 3 and 4). The surface pressure remained at 4 mN/m when the barrier was moved to the maximum area position after the second decompression. These facts suggest that the PDA-UR molecule formed an irreversible monolayer at the air−water interface. This irreversibility is due to the aggregation formation between lipid molecules at the air−water interface through some strong intermolecular interactions.

The aggregate formation of the PDA-UR monolayer was directly observed by Brewster angle microscopy (Figure 6). At low surface pressure (between 0 and 5 mN/m), small islands can be identified in the monolayer topography (Figure 6a). This indicates that PDA-UR lipids started to aggregate together even at relatively low surface pressure. When compressed to higher surface pressure (10−15 mN/m), small islands were united to become larger aggregates (Figure 6b). This means that with the compression of the monolayer, more and more PDA-UR lipid molecules self-assembled together into domain structures. If decompressed at a surface pressure of 20 mN/m, we can clearly see in the video camera that the monolayer "cracked" into smaller pieces and these smaller pieces remained intact at the interface even after the barrier was moved back to the maximum area position. Corresponding to the previous compression/decompression isotherm measurements, the topography of the monolayer observed from the BAM images is additional experimental evidence to demonstrate that PDA-UR lipids formed an irreversible monolayer at the air−water interface.

On the basis of these investigations, we were obliged to reconsider the model of the PDA-UR monolayer to explain the observed experimental results. The following question was asked: Is it possible for PDA-UR molecules to form a similar hydrogen bonding network at the air−water interface like other urea derivatives in the solid state as illustrated in Figure 1? If it does so, then the two alkyl chains in PDA-UR must be in an extended conformation and under this conformation, the PDA-UR can only form a monolayer as illustrated in Figure 7.

One will immediately notice how unusual this monolayer is. The polar moiety of the PDA-UR lipid is actually floating in the air and one of the hydrophobic alkyl chains is in contact with the water subphase. Despite the nontraditional structural feature of the monolayer, this model explains very well the surface pressure−area isotherm measurements and the Brewster angle microscopic studies. First of all, with such a pseudo one-alkyl chain conformation of PDA-UR, the limiting molecular area of PDA-UR should be around 21 Å^2/molecule, equivalent

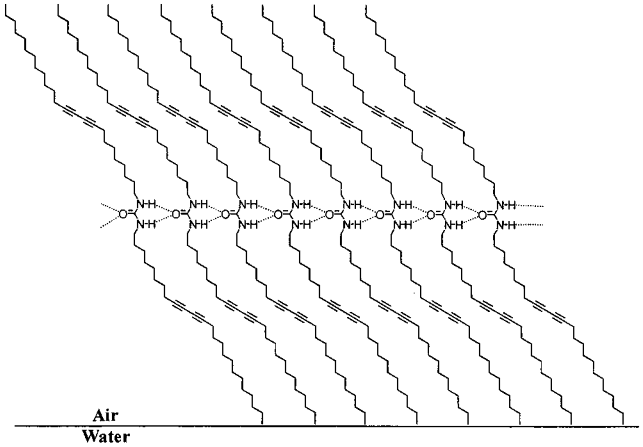


Figure 7. A proposed nontraditional Langmuir monolayer model to explain the surface chemistry properties of PDA-UR.

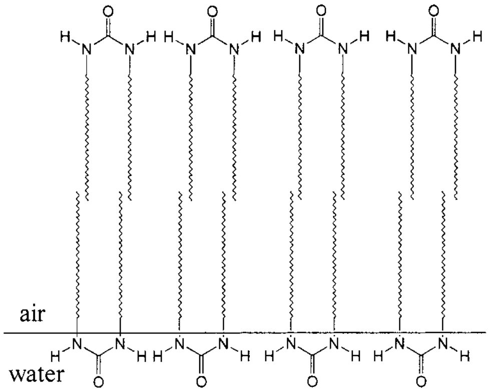


Figure 8. A plausible "double-layer" model of the PDA-UR Langmuir film.

to the area of the cross section of one alkyl chain. Also, with such an extended configuration, it is highly possible for PDA-UR lipids to form a stable and linear hydrogen bonding network, similar to the solid state, leading to the formation of aggregation in the monolayer, as seen from the BAM images. The strength of the hydrogen bonding network, surrounded by an extremely hydrophobic environment, can be so strong that it cannot be disrupted easily once it is formed, leading to the observed irreversibility of the monolayer.

As another very important piece of experimental evidence, we found that the PDA-UR monolayer can be easily deposited onto a hydrophobic glass slide with a deposition ratio near 1 (vertical dipping method, downward). *Most interestingly, it was noticed that the surface of this glass slide with one layer of PDA-UR deposited is still hydrophobic.* On the other hand, the deposition ratio of the PDA-UR monolayer on the hydrophilic glass slide is very poor, lower than 0.2 (upward). These experimental observations clearly tell that *both "sides" of the PDA-UR Langmuir monolayer are hydrophobic,* in complete contradiction to traditional Langmuir monolayers. At the same time, these experimental evidences also eliminate the possibility of PDA-UR forming a double layer at the air−water interface as illustrated in Figure 8. If this is the correct model of the PDA-UR Langmuir film, both sides of the film would be hydrophilic. The FT-IR spectroscopic studies described in the following sections will provide more experimental evidence from the molecular level to eliminate the existence of such a "double-layer" model.

II. Ellipsometry Angle Measurements. To confirm the validation of such a nontraditional Langmuir monolayer model, the measurement of the thickness of the PDA-UR monolayer at the air−water interface is critical. Since if the PDA-UR monolayer configuration is as presented in the traditional Langmuir monolayer model (Figure 3), then the thickness of the monolayer will be close to that of the PDA monolayer. On the other hand, if the proposed nontraditional monolayer model is correct, then the thickness of the PDA-UR monolayer will be almost twice that of the PDA monolayer. We have used the ellipsometry technique[8,9] to measure the thickness of the PDA and the PDA-UR monolayers directly at the air−water interface. The change of the ellipsometric angle Δ is shown along with the change of surface pressure during the compression of the monolayer (Figure 9a,b). The change of another ellipsometric angle ψ (isotherm not shown here) was also monitored and used to estimate the layer refractive index and the thickness.

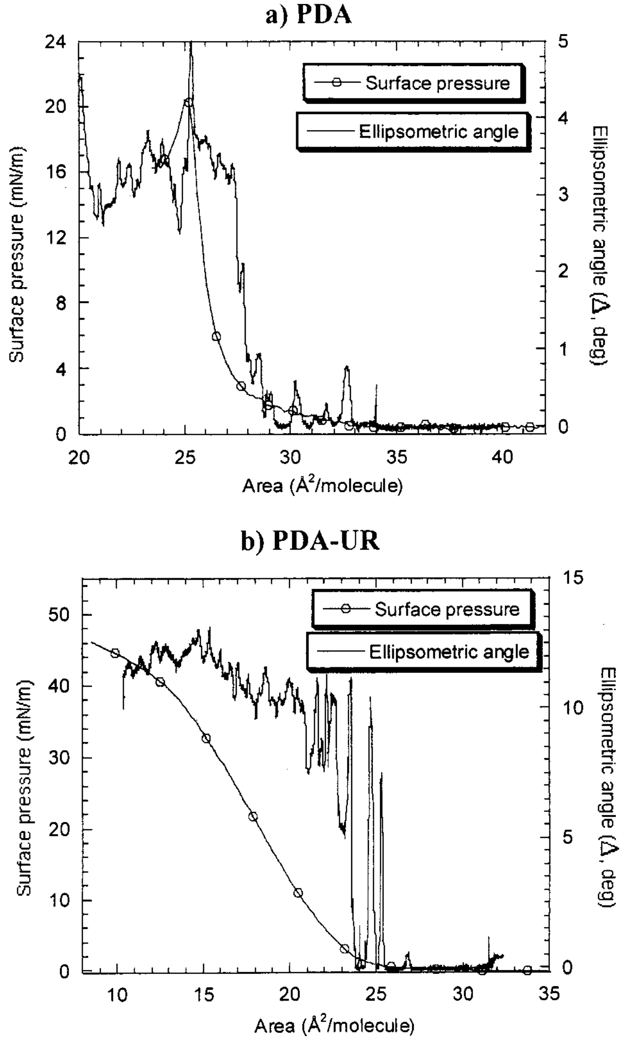


Figure 9. The ellipsometry angle (△)−area isotherms of PDA (a) and the PDA-UR (b) monolayer at the air−water interface.

As to the PDA monolayer, the change of ψ is estimated as 0.024 ± 0.005° and the change of Δ is 3.3 ± 0.1°, which gives the following PDA monolayer parameters:

$$n_{\mathrm{PDA}} = 1.44 \pm 0.03$$

$$d_{\mathrm{PDA}} = 3 \pm 1\ \mathrm{nm}$$

n_{PDA} is the refractive index of the PDA monolayer and d_{PDA} is the thickness of the monolayer. The measured thickness of the PDA monolayer, 3 nm, corresponds very well with the length

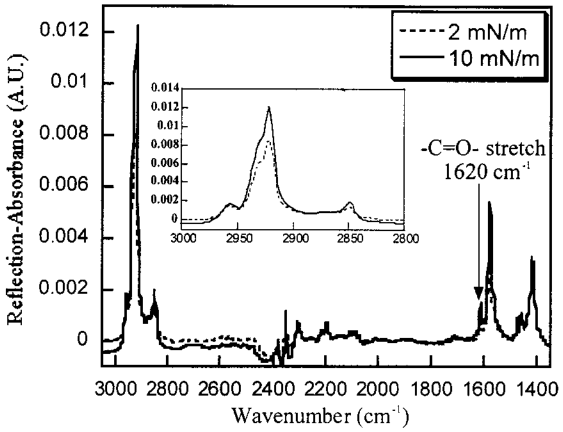


Figure 10. The FT-IR spectra of one layer PDA-UR Langmuir−Blodgett films deposited onto a flat gold surface at two different surface pressures. The inserted smaller figure is the enlargement of the spectra region from 3000 to 2800 cm^{-1}.

of the extended PDA molecule obtained from its CPK model (3 nm). In the meantime, from the ellipsometric angle−area isotherm of the PDA-UR monolayer, the refractive index and the thickness were estimated as:

$$n_{\mathrm{PDA-UR}} = 1.47 \pm 0.03$$

$$d_{\mathrm{PDA-UR}} = 7 \pm 1\ \mathrm{nm}$$

The thickness of the PDA-UR monolayer is roughly the twice that of the PDA monolayer. This measured thickness also corresponds very well to the calculated length of the PDA-UR molecule (7 nm, from CPK model), with its extended conformation as illustrated in Figure 7. The ellipsometry measurements unambiguously suggest that PDA-UR molecules organized at the air−water interface with the two side chains fully extended and standing almost perpendicular to the water surface, formed a monolayer as proposed in the model. It needs to be mentioned that the large jumps in Δ of the PDA-UR monolayer are not experimental noise, but rather are due to the compressed layer islands, as observed in the Brewster angle microscopic studies.

III. FT-IR Spectroscopic Studies. Furthermore, we have used the FT-IR spectroscopy to determine the molecular orientation of PDA-UR molecules in the monolayer. The IR spectra of one layer PDA-UR Langmuir−Blodgett films deposited at a surface pressure of 2 and 10 mN/m on a flat gold surface were presented in Figure 10. From the IR spectra, two striking features regarding the C═O stretching band of the PDA-UR molecule were noticed immediately. First of all, in both the solid state (KBr pellet, spectra shown in Supporting Information) and the Langmuir−Blodgett films at two different surface pressures (Figure 10), this band appeared at 1620 cm^{-1}. Normally, the C═O stretching band appears above 1650 cm^{-1} for most organic molecules.[14] When the carbonyl group is hydrogen bonded, this band will shift toward lower wavenumber, as reported in previous studies.[3,15,16] We also noticed that in a diluted chloroform solution of PDA-UR (10^{-4} M), this band appeared at 1690 cm^{-1}.[17] These data strongly suggest that compared to the free solution, the PDA-UR molecules formed a hydrogen bonding network in both the solid state and the Langmuir monolayer, and the C═O stretching band shifted to lower wavenumber.

Table 2. The Calculated Molecular Orientation of PDA-UR in One Layer Langmuir−Blodgett Film

surface pressure (mN/m)	antisymmetric CH$_2$ (deg)	symmetric CH$_2$ (deg)	γ, deg
2.0	74	83	17.5
10.0	73	82	18.9

The second feature is the intensity of the C═O stretching band. It is found that in the PDA-UR Langmuir−Blodgett film, the intensity of this band is very weak, while in the solid state, this is a very strong band, as usually observed from molecules with carbonyl groups.[14] It is known that the RAS-mode IR measurement is only sensitive to vertically oriented vibrations.[18] In our nontraditional monolayer model as presented in Figure 7, the carbonyl groups are oriented parallel to the water surface and the spectrometer cannot detect this vibration band sensitively, leading to the observed low intensity of this vibration band. This spectral feature is another strong support of the proposed "one-layer" model. On the other hand, if the PDA-UR Langmuir film adopts the "double-layer" configuration as presented in Figure 8, the C═O group will be oriented vertically to water surface and the intensity of the C═O stretching band should be much stronger.

The molecular orientation of the PDA-UR monolayer has been calculated based on the IR spectra of its Langmuir−Blodgett films at two different surface pressures. Comparing the spectra from surface pressures of 2 and 10 mN/m, the intensity is slightly increased with the increase of surface pressure, but the molecular orientation itself is not affected by the compression significantly. This suggests that the PDA-UR monolayer is quite stable in the surface pressure range of 2−10 mN/m, corresponding to the surface pressure−area isotherm studies. With the parameters as described in the Experimental Section, calculations were performed. The results are summarized in Table 2. γ is the tilt angle of a hydrocarbon chain from the normal of the water surface, which is deduced from the two orientational angles of the antisymmetric and symmetric CH$_2$ stretching vibration modes. From this tilt angle (17.5 and 18.9° at surface pressures of 2 and 10 mN/m, respectively), one can see *that the PDA-UR molecule has a nearly perpendicular stance to the surface*, although the orientation of the antisymmetric CH$_2$ stretching mode is slightly tilted. The molecular orientation of PDA-UR in Langmuir−Blodgett films by FT-IR spectroscopic studies also clearly supports the validation of the proposed nontraditional PDA-UR monolayer model.

IV. Photopolymerization ofthe PDA-UR Langmuir Film. As an original purpose of this study, the photopolymerization of PDA-UR molecules at the air−water interface was investigated. The UV−vis absorption spectra of the polymerized PDA-UR monolayer are presented in Figure 11. From the chromatic properties of polymerized PDA-UR monolayer, a few more important conclusions are made. First of all, it was noticed that the maximum absorbance at 660 nm of the polymerized monolayer after irradiation of 600 s is about 0.03. It was reported previously that the maximum absorbance at 640 nm of the polymerized PDA monolayer before the color transition is between 0.01 and 0.02.[13,19] The observed maximum absorbance

---

(14) Daimay, L. Y.; Norman, B. C.; William, G. F.; Jeanette, G. G. In *The Handbook of Infrared and Raman Characteristic Frenquencies of Organic Molecules*; Academic Press: New York, 1991.

(15) Bohanon, T. M.; Denzinger, S.; Fink, R.; Paulus, W.; Ringsdorf, H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1033.

(16) Huo, Q.; Dziri, L.; Desbat, B.; Russell, K. C.; Leblanc, R. M. *J. Phys. Chem. B* **1999**, *103*, 2929.

(17) Huo, Q. Ph.D. Thesis, Design, synthesis and application of hydrogen bond directed molecular receptors and supramolecular self-assemblies, University of Miami, Coral Gables, FL, 1999, pp 22−23.

(18) Umemura, J.; Kamata, T.; Kawai, T. *J. Phys. Chem.* **1990**, *94*, 62.

(19) Kuriyama, K.; Kikuchi, H.; Kajiyama, T. *Langmuir* **1998**, *14*, 1130.

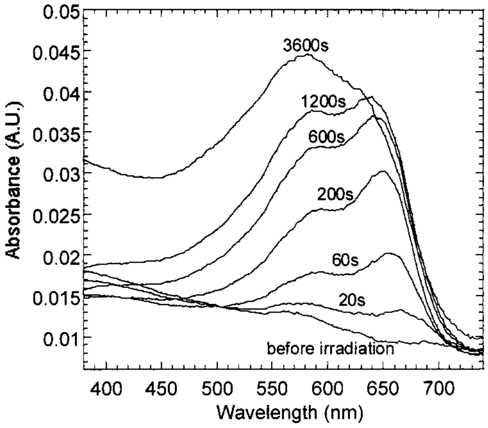


Figure 11. The UV−vis absorption spectra of the PDA-UR monolayer on the water subphase after a certain period of photopolymerization.

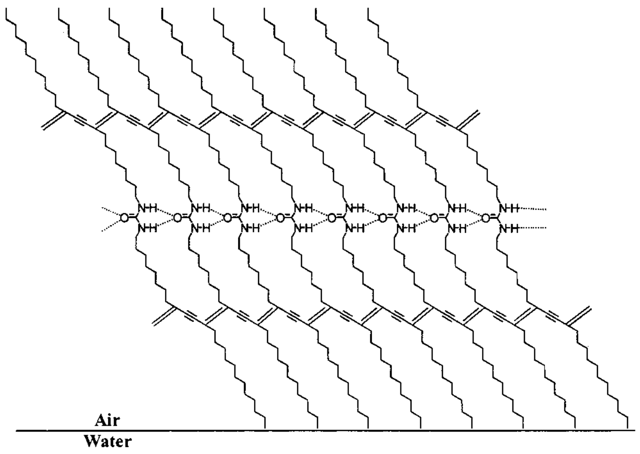


Figure 12. The ultra rigid structure of the polymerized PDA-UR monolayer due to the formation of the linear hydrogen bonding network and "dual polymerization" of diacetylene groups on the two sidearms of PDA-UR.

from the PDA-UR monolayer is approximately twice that of the PDA monolayer. This result is an indirect experimental support of the monolayer model presented in Figure 7. Since after the polymerization there are virtually two polydiacetylene chains formed in the monolayer (Figure 12), the absorbance of the monolayer is doubled compared to that of the PDA monolayer.

Second, the polymerized PDA-UR monolayer only exhibits a blue-form absorption band (660 nm), instead of undergoing a transition from blue to red (640 to 540 nm), as observed from PDA and other PDA derivative monolayers.[6,13,19] Previously, we have reported the hydrogen-bonding effect on the chromatic properties of diacetylene lipid monolayers.[6,20] Details are not described here. In summary, with the existence of a strong hydrogen-bonding network formed between lipid molecules at the air−water interface, the polydiacetylene backbone can maintain its linear structure even under elongated photoirradiation conditions. With such a linear chainlike structure, the π electrons in the polydiacetylene backbone are highly conjugated and the film remains as a blue form during the elongated photoirradiation. A similar phenomenon is observed here with the PDA-UR monolayer. Apparently, the hydrogen-bonding network formed between the urea functional groups is a strong force to maintain the blue form polydiacetylene structure. Furthermore, we would like to address that the hydrogen-bonding network and the "dual polymerization" of diacetylene groups from two sidearms make the PDA-UR monolayer become a highly cross-linked and ultra rigid polymer network as illustrated in Figure 12. With the unique physical and electronic properties of polydiacetylene compounds, such as the large nonlinear optical susceptibilities comparable to inorganic semiconductors with ultrafast responses,[21,22] this polymerized PDA-UR thin film may find some interesting potential applications as a new material.

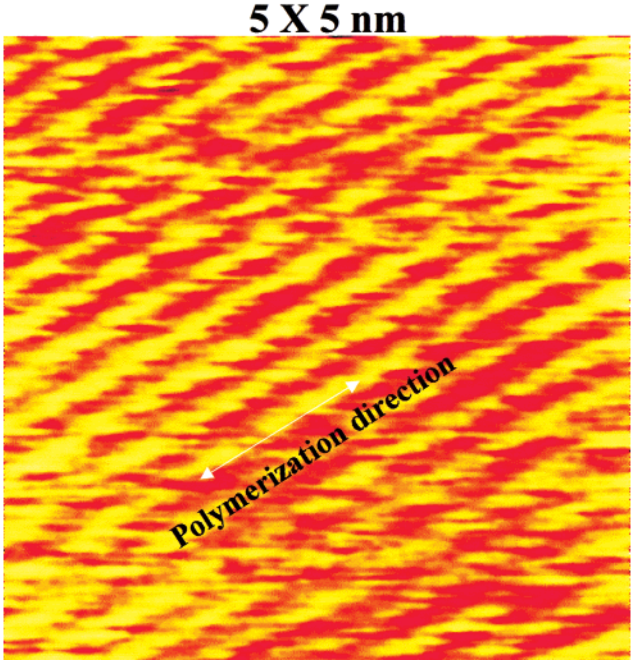


Figure 13. The STM image of the polymerized PDA-UR monolayer deposited onto freshly cleaved graphite at a surface pressure of 20 mN/m (Langmuir−Schaefer method, deposition ratio ~1.0).

The topography of the polymerized PDA-UR Langmuir film was observed by scanning tunneling microscopy (STM).[23] The polymerized PDA-UR monolayer at a surface pressure of 20 mN/m was transferred onto freshly cleaved graphite (HOPG, ZYB grade, Advanced Ceramics, Lakewood, OH). Highly organized linear strip-like structures can be clearly seen from the image (Figure 13). When scanned in larger area, same topography was observed, except that the number and length of the strips in the image window increases accordingly. The long linear strips seen in the STM image represent the polymerized PDA-UR chains viewed from the top of the monolayer, with the polymerization direction as illustrated in the figure. The topographical feature of the polymerized PDA-UR monolayer is direct evidence to show that, indeed, the PDA-UR molecules "stood up" at the air−water interface during the compression, and formed a monolayer as we proposed in this study.

Conclusions

On the basis of these experimental studies, we concluded that the PDA-UR molecules formed an unusual monolayer at the

---

(20) Huo, Q.; Wang, S.; Pisseloup, A.; Verma, D.; Leblanc, R. M. *Chem. Commun.* **1999**, 1601.

(21) Prasad, P. N.; Williams, D. J. In *Introduction to Nonlinear Optical Effects in Molecules & Polymers*; John Wiley & Sons: New York, 1991; pp 231−235.

(22) Palchettri, L.; Li, Q.; Giorgetti, E.; Grando, D.; Sottini, S. *Appl. Opt.* **1997**, *36*, 1204.

(23) The instrument used in this study is a Nanoscope II STM, Digital Instruments, Santa Babara, CA. The parameters for the image are as follows: scan size 5 × 5 nm, Z range 0.52 nm, bias voltage 161.13 mV, set current 1.0 nA, scan rate 2.48 Hz, integral gain 1.5, and proportional gain 1.0.

air–water interface with their polar moieties suspended in the air and the hydrophobic tail in contact with the water. It was reported previously by Rice's research group[24] that a pure fluorinated hydrocarbon chain *without any polar moieties* can also form a stable monolayer at the air–water interface, through the strong van der Waals interactions between the fluorinated alkyl chains alone. His study has demonstrated that *it is possible for the hydrophobic alkyl chain to be in contact with the water surface in a unique Langmuir monolayer environment*. In our work reported here, we clearly show that the traditional configuration of the Langmuir film *(water–polar groups ↔ alkyl chains–air)* can be flipped over to a completely opposite direction *(water–alkyl chains ↔ polar groups–air)*. Our discovery not only provided a new possibility to design nontraditional supramolecular-like Langmuir and Langmuir–Blodgett films, but also brought up some new interesting insights into the basic study of this research field.

Supporting Information Available: FT-IR spectra of PDA-UR in KBr pellet (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA984158J

---

(24) Li, M. Y.; Acero, A. A.; Huang, Z. Q.; Rice, S. A. *Nature* **1994**, *367*, 151.